A triad of rhenium-mediated transformations[¶]

JAYDIP GANGOPADHYAY[a], SAMIR DAS[a], SUMAN SENGUPTA[a],
INDRANIL CHAKRABORTY[a] and ANIMESH CHAKRAVORTY*[,a,b]

[a]Department of Inorganic Chemistry, Indian Association for the Cultivation
of Science, Kolkata 700 032, India
[b]Jawaharlal Nehru Centre for Advanced Scientific Research,
Bangalore 560 064, India
e-mail: icac@mahendra.iacs.res.in

Abstract. The title transformations are oxygen atom transfer, twin isomerization and regiospecific imine oxidation. *Bis*pyridyldiazole ligands have furnished new oxygen atom transfer reagents of coordination type $Re^{V}OCl_3(NN)$ which undergo a slower transfer to PPh_3 than the corresponding azole reagents. The rate of twin isomerization (linkage and geometrical) of meridional azole complexes of coordination type $Re^{III}(OPnP)Cl_3(NN)$ to facial $Re^{III}(PnPO)Cl_3(NN)$ decreases rapidly as n increases in the interval 1–4 (PnP is $Ph_2P(CH_2)_nPPh_2$). An a-diimine chelate of type $Re^{V}(NPh)Cl_3(NN)$ is shown to undergo facile oxidation to the corresponding iminoamide complex $Re^{VI}(NPh)Cl_3(NN)$ upon treating with dilute nitric acid. The reaction proceeds via regiospecific nucleophilic addition of water to the more polarized imine function.

Keywords. Rhenium-mediated transformations; oxygen atom transfer; linkage-cum-geometrical isomerization; regiospecific imine oxidation.

1. Introduction

During the last five years or so, one of the areas that we have been engaged in is the synthesis and characterization of rhenium compounds that display interesting reactivity.[1–8] A selection of new results will be briefly reported in this paper.

2. Experimental

2.1 *Synthesis*

*Bis*pyridyldiazoles (L) were prepared by reported methods[9] and $Re^{V}OCl_3(L)$ synthesized by reacting $Re^{V}OCl_3(PPh_3)_2$ with L in benzene in 1:1 mole ratio at room temperature. The $Re^{III}(OPPh_3)Cl_3(L)$ complexes were prepared by stirring $Re^{V}OCl_3(L)$ and PPh_3 in 1:3 mole ratio in dichloromethane at room temperature. The $Re^{III}(OPnP)Cl_3(pbo)$ complexes were similarly prepared from $ReOCl_3(pbo)$ and PnP. The $Re(PnPO)Cl_3(pbo)$ isomer was formed upon keeping solutions of $Re(OPnP)Cl_3(pbo)$ in dichloromethane at room temperature.

[¶]Dedicated to Professor C N R Rao on his 70th birthday
*For correspondence

The concerned *a*-diimine (diim) ligand was prepared by a reported method[10] and Re^{V}(NPh)Cl$_3$(diim) resulted upon boiling a mixture of ReOCl$_3$ (diim) and excess aniline in toluene. The complex Re^{VI}(NPh)Cl$_3$(imam) were obtained by stirring Re(NPh)Cl$_3$(diim) with 0·5 N nitric acid in acetonitrile at room temperature.

In general, the compounds were characterized with the help of elemental analysis, spectra (IR, UV-Vis, ^{1}H NMR) and cyclic voltammetry. The Re^{VI}(NPh)Cl$_3$(imam) complex is paramagnetic ($5d^1$) and display sextet ($I = 5/2$) EPR spectrum.

2.2 *Rate measurements*

The reaction (1) below in §3.1 was followed spectrophotometrically (thermostated cell compartment) in the usual manner by measuring the absorbance as a function of time.[8] The rate of twin isomerisation was also determined spectrophotometrically following a reported procedure.[11,12]

2.3 *X-ray structure determination*

Data on single crystal crystals of the complexes ReOCl$_3$(bptd) and Re(NPh)Cl$_3$(diim) were collected on a Nicolet R3m/V four-circle diffractometer with graphite monochromated Mo-K*a* radiation in the 2*q* range 3–50°. Calculations were performed using the SHELXTL^{TM} V5·03[13] program package. Further details will be reported elsewhere.

3. Results and discussion

3.1 *Oxygen atom transfer*

A notable reaction of Re^{V}O species is oxygen atom transfer to oxophilic substrates.[1–3,7,8,14] Transfer reactions promoted by enzymatic oxo sites based on iron, molybdenum and tungsten are important in the chemistry of life.[15,16] Rhenium is not a biometal in the same sense, but as an element in the periodic group next to that of molybdenum and tungsten, transfer reactions involving Re^{V}O are of value as potential models.[3]

The N,N-chelation of Re^{V}O by pyridyl ligands have been of interest to us. In pyridine-2-aldimines the second nitrogen site is located in an acyclic substituent pendent from the 2-position of the pyridine ring.[3] The use of heterocyclic substituents can add a new dimension to pyridyl-Re^{V}O chemistry and a beginning was made utilizing pyridylbenzazoles, **I** such as pbo and pbt to construct the oxygen atom transfer reagents ReOCl$_3$(pbo) and ReOCl$_3$(pbt).[8] The synthesis of the new reactive chelates ReOCl$_3$(bpod) and ReOCl$_3$(bptd) has now been achieved from ReOCl$_3$(PPh$_3$)$_2$ and the *bis*-pyridyldiazoles (bpod and bptd), **II**.
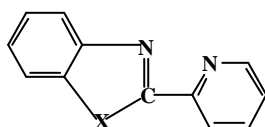
X = O   pbo
X = S   pbt

I
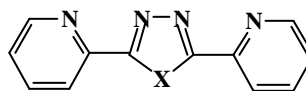
X = O   bpod
X = S   bptd

II

The structure of ReOCl$_3$(bptd) has been determined and is depicted in figure 1. The observed Re–O distance, 1·699(13) Å, corresponds to triple bonding.[8] In dichloromethane solution, ReOCl$_3$(bpod) and ReOCl$_3$(bptd) react smoothly with PPh$_3$, furnishing the corresponding phosphine oxide species, which have been isolated and characterized. The rate of reaction (1), where L is bpod/bptd, has been determined spectrophotometrically.

$$\text{ReOCl}_3(\text{L}) + \text{PPh}_3 \xrightarrow{\ k\ } \text{Re(OPPh}_3)\text{Cl}_3(\text{L}). \tag{1}$$
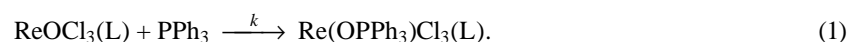
Under pseudo-first-order condition (excess PPh$_3$) the rates are proportional to the concentration of ReOCl$_3$(L) and the observed rate constants are in turn proportional to the concentration of PPh$_3$. The process is thus second order in nature:

$$\text{rate} = k\ [\text{ReOCl}_3(\text{L})][\text{PPh}_3]. \tag{2}$$

Relevant rate constant data at 302 K are collected in table 1.

Certain significant trends emerge from the data. The heteroatom electronegativity order O > S makes the bpod and pbo reagents (X = O) more potent oxidants compared to the corresponding X = S species. Also the present diazole reagents are sluggish oxidants compared to the azole species. In effect the diazole ligands are less electron withdrawing than the azole ligands. This is consistent with the reaction model[8] shown in scheme 1 where full and broken lines respectively represents coordinate covalent bonds and weak links. Following attack on p^*(ReO) orbitals by the phosphine lone-pair, the p bonds are

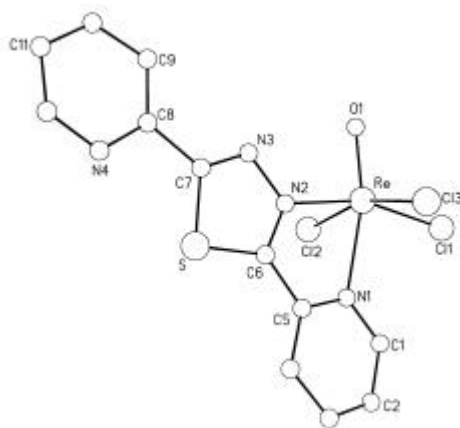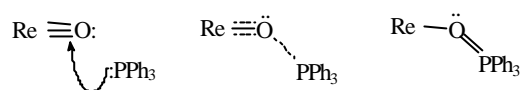**Figure 1.** Perspective view and atom-labelling scheme of ReOCl$_3$(bptd).

Table 1. Rate constant data at 302 K.

| Compounds	$10^3\,k\ \text{M}^{-1}\,\text{s}^{-1}$
ReOCl$_3$(bpod)	1·59 (0·05)
ReOCl$_3$(bptd)	1·34 (0·06)
ReOCl$_3$(pbo)	4·18 (0·02)[a]
ReOCl$_3$(pbt)	2·00 (0·06)[a]

[a]Data taken from ref. [8]

Scheme 1.

weakened and a O….P link is established (transition state). In the end, the P=O bond remains coordinated to the metal.

3.2 *Twin isomerization*

It has been demonstrated[6,11,17] that displacement of $OPPh_3$ by PPh_3 in complexes of type $Re(OPPh_3)Cl_3(NN)$ furnishes $Re(PPh_3)Cl_3(NN)$. The process is attended with isomerization from meridional, **III** to facial, **IV** geometry which is stabilised by back-bonding (the
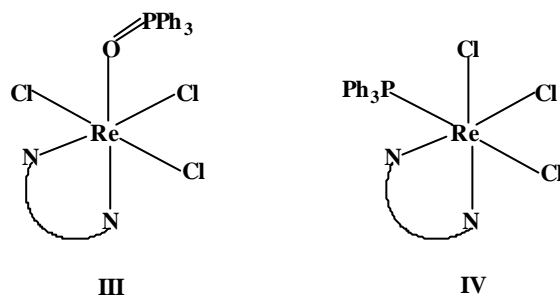

NN coordinating ligands are pyridine-2-aldimines[6] or azoheterocycles[11,17]). When excess of diphosphines of type **V** (abbreviated as PnP) are reacted with $ReOCl_3(NN)$, oxygen atom transfer affords **VI**, which has a dangling phosphine function. Left in solution, the **VI** ($n = 1$) complex undergoes spontaneous intramolecular transformation to **VII**. This process is essentially a twin isomerization – both linkage (ReOP1P $\rightarrow$ ReP1PO) and geometrical (meridional $\rightarrow$ facial). However, the **VI** ($n > 1$) species are unreactive presumably due to the distance factors.[11,12]
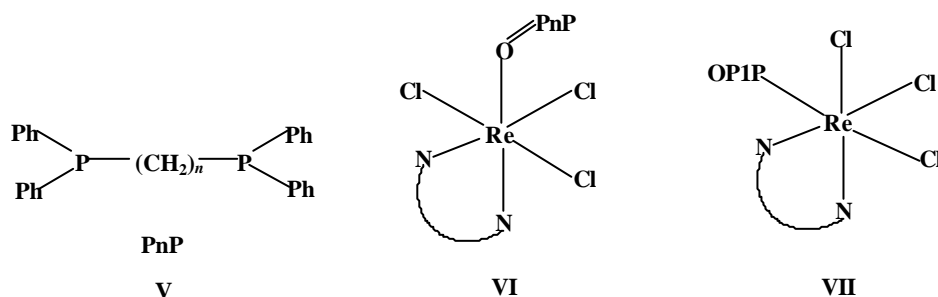
We have been searching for a system of type **VI** where the twin isomerization process is observable for a number of *n* values. This has now been realized in the species of type

Re(OPnP)Cl$_3$(pbo). The value of n was varied from 1–4 and all the species displayed twin isomerization (**VIII → IX**), the rate of which diminished progressively as n increased. Preliminary rate data ($n = 1$, 0·0051; $n = 2$, 0·0024; $n = 3$, 0·0010; $n = 4$, 0·0003 min^{-1} at 310 K) suggests that the decrease is approximately exponential. Further scrutiny in terms of conformations of the alkyl chain is in progress.

$n = 1–4$

VIII

$n = 1–4$

IX
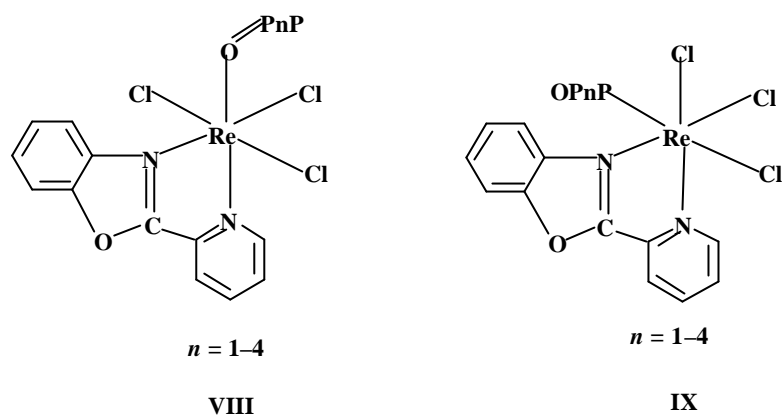
3.3 *Regiospecific imine oxidation*

We are currently investigating the binding of *a*-diimine ligands to different oxidation states of rhenium. Here we are concerned with Re^V(NPh)Cl$_3$(diim), **X**, the structure of which is shown in figure 2. An interesting preliminary finding is that **X** undergoes facile oxidation upon treatment with dilute nitric acid in acetonitrile solution furnishing the corresponding iminoamide complex Re^{VI}(NPh)Cl$_3$(imam), **XI**. Structural studies have revealed that the imine function *trans* to the chloride ligand is selectively oxidized.
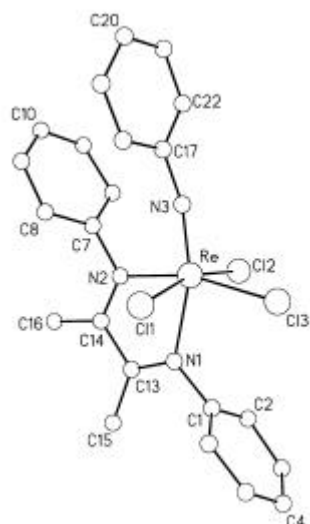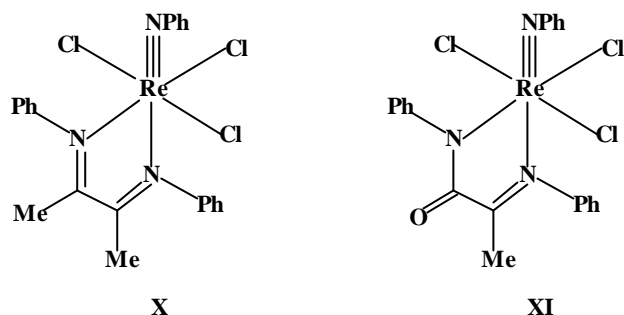

**Figure 2.** Perspective view and atom-labelling scheme of Re(NPh)Cl$_3$(diim).

The crucial step in this transformation is believed to be[3–6,18] nucleophilic addition of water at an imine function of $Re^{VI}(NPh)Cl_3(diim)^+$ formed by oxidation of **X** by nitric acid. The intermediate **XII**, thus generated can react by the induced electron transfer route[19] finally furnishing **XI**. The observed regiospecificity is consistent with this pathway since in **X** the Re–N bond *trans* to the chloride ligand is significantly shorter (by ~0·15 Å) than that *trans* to the NPh ligand. This trend would continue even on metal oxidation. Thus the imine function *trans* to the chloride ligand is more polarized and subject to more facile water attack. It is this function that becomes the exclusive site of amide formation. Further work is in progress.
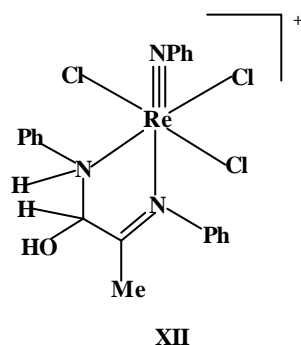
4.   Conclusion

New oxygen atom transfer reagents based on chelation of Re^VO by *bis*pyridyldiazoles have been synthesized and their transfer reactions with PPh_3 scrutinized. The rate of twin isomerization of $Re(OPnP)Cl_3(pbo)$ rapidly diminishes as *n* increases. The $Re(NPh)Cl_3$ (diim) complex undergoes oxidation at the more polarized imine function furnishing $Re(NPh)Cl_3(imam)$.

References

1. Rowbottom J F and Wilkinson G 1972 *J. Chem. Soc.*, *Dalton Trans.* 826
2. Bryan J C, Stenkamp R E, Tulip T H and Mayer J M 1987 *Inorg. Chem.* **26** 2283
3. Dirghangi B K, Menon M, Pramanik A and Chakravorty A 1997 *Inorg. Chem.* **36** 1095
4. Dirghangi B K, Menon M, Banerjee S and Chakravorty A 1997 *Inorg. Chem.* **36** 3595
5. Banerjee S, Dirghangi B K, Menon M, Pramanik A and Chakravorty A 1997 *J. Chem. Soc.*, *Dalton Trans.* 2149
6. Bhattacharyya S, Banerjee S, Dirghangi B K, Menon M and Chakravorty A 1999 *J. Chem. Soc.*, *Dalton Trans.* 155
7. Seymore S B and Brown S N 2000 *Inorg. Chem.* **39** 325
8. Gangopadhyay J, Sengupta S, Bhattacharyya S, Chakraborty I and Chakravorty A 2002 *Inorg. Chem.* **41** 2616
9. Geldard J F and Lions F 1965 *J. Org. Chem.* **30** 318
10. Kliegman J M and Barnes R K 1970 *Tetrahedron* **26** 2555
11. Bhattacharyya S, Chakraborty I, Dirghangi B K and Chakravorty A 2001 *Inorg. Chem.* **40** 286
12. Bhattacharyya S, Chakraborty I, Dirghangi B K and Chakravorty A 2000 *Chem. Commun.* 1813
13. Sheldrick G M 1994 SHELXTL™, Version 5.03; Siemens Analytical Instruments, Madison, WI
14. Banerjee S, Bhattacharyya S, Dirghangi B K, Menon M and Chakravorty A 2000 *Inorg. Chem.* **39** 6, and references therein
15. Hille R 1996 *Chem. Rev.* **96** 2757
16. Holm R H, Kennepohl P and Solomon E I 1996 *Chem. Rev.* **96** 2239
17. Chakraborty I, Bhattacharyya S, Banerjee S, Dirghangi B K and Chakravorty A 1999 *J. Chem. Soc.*, *Dalton Trans.* 3747
18. Menon M, Pramanik A and Chakravorty A 1995 *Inorg. Chem.* **34** 3310, and references therein
19. Taube H 1973 *Electron transfer reaction of complex ions in solution* (New York: Academic Press) p. 73